"Dear Rusty"
Answers to Corrosion Inquiries

by Rusty H. Fingers

Dear Rusty,

I recently had occasion to replace some steel parts that had corroded over time. Because I know stainless steel won't corrode (and I had extra money in my budget at the end of the year), I felt that it should certainly be worth a few extra dollars to upgrade to this material of construction. But, I want to be sure I get a good quality stainless steel. Would you clarify some things for me?

I talked to some of the guys I work with to see what they knew about stainless steel. One told me that I could tell a good quality stainless because a magnet wouldn't be attracted to it. However, another friend told me that he'd seen some stainless steel with rust on it even though a magnet wouldn't pick it up; so, the magnet test probably isn't a very reliable quality test. A third said that he makes knives as a hobby and that the best stainless he has found is 420 stainless and that it is attracted to a magnet; but, he says his brother-in-law, who works at a chemical plant, never uses it in his work because it isn't corrosion resistant enough. They use a lot of 304L and 316L and sometimes something called duplex. When I called a company that sells stainless stock, the clerk started talking about ferritics and austenitics etc., which meant nothing to me. It seems the more people I talk to about stainless steel, the more confused I get.

I didn't realize stainless steel was such a complex animal. Which of these people is correct, and what's the significance of what they're telling me?

Sincerely,
Confused

Dear Confused,

Stainless steel selection and use can be rather involved. Fortunately, equipment vendors usually do some of the work for you; they make their equipment out of a limited number of alloys (hopefully including the one you need) from which you get to choose. I'll present below a smattering of issues to consider when choosing a stainless steel, though these will by no means be necessarily all of the considerations. If, after reading this, you have specific followup questions, please feel free to use the contact information at the end of this article. I hope that by then we can call you by your first name, which I trust will be Les.

To begin, stainless steel is not one single alloy but well over 100 alloys, including standard and non-standard or proprietary types. So, stainless steel is not a complex animal – it's a complex herd. Furthermore, stainless steels (stainlesses) do corrode – sometimes in some "interesting" ways. Let's start by seeing what constitutes a stainless steel and by grouping this herd into five families with similar characteristics.

Stainless Steel Metallurgy, or, How to Build a Stainless Reputation

Basically, to make a stainless steel, simply add at least 10 % – 11% chromium to a steel melt. Steels with less than this amount of chromium do show some improved properties, but these are termed chromium-steels, not stainless steels. Beginning at around the 10 % – 11% chromium addition, the resulting steel alloy demonstrates markedly improved corrosion performance in oxidizing environ-ments due to a thin, self-healing, passive (non-reactive) oxidized chromium rich film that forms on the surface. Stainless steel oxidation resistance improves with further chromium additions up to typically about 30%.

To keep it simple, without going "chemist" on you (I'm certain that'll get a "reaction" out of some people), an oxidizing environment is one that will typically connect oxygen, a group of atoms containing oxygen, or even some non-metal to the metal on the surface of the alloy. Whereas such a reaction would pull the metal of a susceptible alloy off the surface, stainless steel essentially holds on to the attaching species and forms a protective or passive film with it. This passive or non-reactive film in air is typically a chrome oxide rich surface. In an unusual environment or solution, one would expect the passive film to modify itself in accordance with the chemistry of the solution or gaseous environment to which it is exposed.

Since their initial development at the turn of the 1900s in France, England, and Germany, and their commercial production and use in the U.S. in the 1920s, the stainless steel alloys have also benefited from a number of other alloying elements, creating new compositions to meet special performance requirements. Two elemental additions of particular significance to one interested in corrosion are nickel and molybdenum; the effect of these and a few other additives will be described below. Moreover, refinements in steel-making that have improved purity and precise additions have helped advance stainless steel technology as well. Today, stainless steel technology is quite sophisticated (translation: big bucks for some consultants).

Stainless steels can be grouped together into several general classifications based on their microstructure (crystals and particles seen under the microscope). These are:

- Ferritic stainlesses
- Austenitic stainlesses
- Martensitic stainlesses
- Precipitation hardening stainlesses
- Duplex stainlesses

Although we will be talking mainly about wrought (sheet, bar stock, and the like that have been worked) stainlesses below, it is important to note that there are cast stainlesses as well. These may also be grouped into categories described above. However, they have their own designations (e.g., American Casting Institute or ACI designations), and some cast alloys will at times be similar in composition and performance to a wrought product. For instance, CF8M will be very similar in composition to 316 stainless, and CF3M will be similar to 316L.

Ferritic stainlesses are very "basic" iron-chromium stainlesses. These include 430 and 434 stainlesses used in automotive trim and 409 stainless used for automotive mufflers, catalytic converters, and exhaust systems. They have a microstructure of ferrite (pure iron in body-centered cubic crystalline form) and carbides. They are magnetic. They can be difficult to weld without affecting ductility (ability to bend, stretch, and generally deform without breaking), generally have limited toughness (i.e., susceptibility to fracture upon sudden impact), and they are usually found in the form of sheets or lighter-gauge tubulars.

Austenitic stainlesses have austenite stabilizers such as nickel, manganese, and nitrogen added to the melt—I will now to translate from metallurgist into English.

Many people (i.e., non-metallurgists, also known as real people) do not realize that, if a block of steel is suspended by a magnet and heated, a point will be reached at which the hot but still solid steel will drop from the magnet. This is because the basic crystalline structure of the steel above a given temperature changes from the body-centered cubic ferrite, which is attracted to a magnet (a property called ferromagnetism), to the face-centered cubic austenite, which is not attracted to a magnet. However, the block of steel will revert to a ferrite microstructure and regain its ferromagnetism upon cooling. By adding materials called austenite stabilizers to a heat of stainless steel, it is possible to retain this austenite phase at room and lower temperatures. As a result, austenitic stainlesses are not attracted to a magnet. Having said that, since every rule has an exception (including this one?), you will see below that some austenitic stainless pieces may show some attraction to a magnet even though austenite doesn't.

Austenitic stainlesses have excellent corrosion resistance and are used fairly extensively in the chemical processing industry and the food industry, as well in many other applications. Probably the two best known versions are 304L and 316L; austenitic stainlesses usually carry a 300 designation (exceptions include 201 stainless). Austenitics are the most readily welded of the stainless, and they

are highly ductile and have excellent toughness, even at low temperatures. However, they have relatively low yield strength and rapidly work-harden; anyone who has tried to machine a 300 series stainless at the wrong speed or feed rate knows how work-hardening can wear down tools rapidly and make machining difficult. Austenitic stainlesses also conduct heat relatively poorly (i.e., low coefficient of thermal conductivity) compared to some other metals and expand relatively much upon heating (i.e., high coefficient of thermal expansion).

As I indicated above, austenitic stainlesses will sometimes show some attraction to a magnet. First of all, weld beads created from austenitic weld rods will have some ferrite in them and will therefore usually mildly attract a magnet for that reason. The ferrite (at least 3% by volume) has beneficial effects (e.g., reduced susceptibility to solidification and liquation cracking) without usually affecting corrosion behavior. Another common source of magnetic attraction is strain formed martensite (see martensitic stainlesses below) (i.e., cold working austenitic stainlesses in forming them into shape [e.g., in forming a spring] will cause the partial transformation into another microstructure that is also attracted to a magnet).

Martensitic stainlesses are similar to ferritic stainlesses in composition, but they are different in microstructure. Martensitics are known for their heat-treatability. They tend to be hard, strong, and brittle, but can be tempered to have reasonable toughness. They are typically high in carbon with a minimum of chromium. They have a ferritic structure in the annealed (i.e., heat-treated for softness) condition, but develop a martensitic, body-centered tetragonal crystalline structure, after quenching from above a critical temperature, where they may have had an austenitic structure – enough transformations to make David Copperfield jealous. The martensitics include 420 stainless steel, the original cutlery grade stainless. If they contain alloying elements other than chromium, it'll typically be no more than 2 – 3% total. They tend to have limited corrosion resistance since adding more chromium leads to a ferrite structure instead of hard martensite. They may be considered the most difficult of the stainlesses to weld because of the welding thermal cycles (need careful control of preheat and post-weld cooling rates to deal with shrinkage stresses).

Precipitation hardening stainlesses are typically chromium-nickel grades that can be machined in the annealed condition and then heat-treated by the manufacturer to increase hardness. They can be divided into three groups: austenitic, semiaustenitic, or martensitic precipitation hardening types. Intermetallic precipitates (different metals chemically combining and forming particles in the microstructure) of such elements as copper and aluminum formed during heat treatment increase the strength and hardness; in martensitic and semiaustenitic grades, martensite is precipitated by heat-treatment as well. The precipitation hardening stainlesses will typically have higher levels of alloying constituents than the martensitic stainlesses and have corrosion resistance similar to other chromium-nickel grades. Typical alloys such as 15-5 PH (martensitic),

17-7 PH (semiaustenitic), A286 (austenitic), and others, find use in the aerospace industry for fasteners and other applications. Since there are three sub-groups, weldability issues will vary.

Duplex stainlesses have both austenite and ferrite in their microstructures in approximately a 50/50 ratio – like two families sharing one duplex house. Duplex stainlesses will typically have chromium and molybdenum and a significantly lower level of nickel than the austenitic stainlesses to achieve their mixed microstructure. In this way, they are often able to provide much of the corrosion-resistant properties of an austenitic stainless while avoiding their chloride stress corrosion cracking (SCC) susceptibility (see below for some of the "interesting" ways stainlesses corrode). They are strong and generally quite pitting and crevice corrosion resistant; however, they can have their own particular corrosion problems. They are weldable, but welding to maintain base metal qualities can be tricky; the weld needs to maintain the 50/50 austenite/ferrite structure, requiring the welder to carefully juggle a number of variables. They are sometimes used in the chemical processing industry, for CO_2 piping systems, and for some sour-gas down-hole tubing in the petroleum industry. A typical duplex stainless is 2205.

Stainless Alloying Ingredients, or, Why They Couldn't Leave Well Enough Alone

Although all that is needed for a basic stainless steel is sufficient chromium added to a steel melt, other elements are often added as well to improve properties. However, influencing one property sometimes affects others too; alloying can become a delicate balancing act. The following is a simplified description of some of the more important additives.

Chromium

As previously mentioned, this element is largely responsible for that tough, passive film that provides oxidation resistance to the alloy. Increase the amount of chromium and you increase the oxidation resistance, but watch out. Too high a level of chrome can adversely affect mechanical properties, fabricability, weldability, etc.

Nickel

As seen above, the element nickel (no – I don't mean the type in your pocket, though those coins should contain some nickel too) can dramatically affect the microstructure of stainlesses, leading to austenitic stainlesses that aren't attracted to a magnet. From a corrosion standpoint, it also improves the ability to repassivate in somewhat more reducing (the opposite of oxidizing) environments.

Nickel improves mechanical properties and fabricability. It has an interesting affect on chloride SCC susceptibility (see below) of stainless steels—up to about 8% to 10%, nickel increases susceptibility—greater additions then decrease susceptibility. Nickel increases the cost of a stainless steels.

Molybdenum

The most important affect of this element is improved resistance to chloride pitting and crevice corrosion. Please note that I did not say it rendered stainlesses immune to pitting and crevice corrosion. If you thought adding nickel was expensive, this additive will cost you a pretty penny. The main difference between 304 and 316 stainlesses is about 2.5% molybdenum in 316; however, the price of the latter alloy is about 75% greater (depending on the day of the week, cycle of the moon, etc. – alloy prices can fluctuate greatly). Superaustenitics, such as the proprietary AL6XN, contain 6% molybdenum and have outstanding resistance to pitting and crevice corrosion; resistance to chloride stress corrosion cracking (SCC) is also quite good. However, given the 6% molybdenum content along with about 21% chrome and 24% nickel, you can probably guess at the high cost.

Manganese

In stainless steels, manganese performs many of the functions of nickel. Stainlesses with high manganese levels have some interesting properties, including resistance to galling (no, this does not mean they are less irritating – galling is sort of a cold welding phenomenon sometimes experienced by tightly fitting components). Manganese is cheaper than nickel; however, total replacement of nickel is not practical.

Carbon

This element is important in that it can permit hardenability by heat-treatment, as seen above. It can also provide strength in high temperature applications. However, it is otherwise generally detrimental to corrosion resistance (see intergranular attack below). Carbon is also detrimental to toughness in the ferritic grades.

Nitrogen

This common gas that makes up about 79% of our atmosphere helps improve pitting resistance of stainlesses. It can also retard formation of the undesirable chromium-molybdenum sigma phase (bet you're glad to know that). It is also beneficial in strengthening these alloys. In duplex grades, it can increase

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austenite content, diminish chromium and molybdenum segregation, and increase corrosion resistance of the austenite phase. However, nitrogen can be very harmful to the mechanical properties of the ferritic grades.

Sulfur and Selenium

These elements improve machineability. However, corrosion behavior of the alloy may be affected in some environments.

"Interesting" Ways Stainless Steels Corrode

As I said previously, it is a misconception that stainless steels don't corrode. They rely on a thin but tightly adhering passive (i.e., non-reactive) layer (e.g., chromium oxide) and can corrode quite severely if that thin passive layer breaks down and can't repair itself in the given environment. Basically, this passive film will not be able to repair itself in a reducing environment (the converse of an oxidizing environment—see above), and even general corrosion (corrosion across the entire surface) can ensue; however, stainless steels more often suffer localized attack such as pitting and crevice corrosion, especially when chlorides are involved. Chlorides (as found in road salt or ordinary table salt) are very good at finding chinks in the passive armor of stainless steels and are responsible for several localized corrosion phenomena. In the case of austenitic stainlesses, chlorides can cause a form of cracking called chloride SCC (see below). In fact, I was once told by one old timer that when stainlesses were first being introduced into the chemical process industry, people quickly concluded that stainless steels were not very corrosion resistant. That was because everyone was trying to use them in environments where they were not well suited – acid chloride environments – for instance. When they were used in appropriate environments (e.g., nitric acid), stainless steels performed "brilliantly." Let's take a look at some corrosion-related phenomena and relevant markings that one may encounter when dealing with corrosion-resistant stainless steels (especially the austenitics).

Who dropped this stainless – it's cracked! Austenitic stainlesses, used so commonly in the chemical processing industries, in food preparation, etc., are susceptible to a form of corrosion known as chloride SCC. And no, it doesn't happen because someone drops the part. It's a true form of corrosion. It has even been shown experimentally that cathodic protection can stop it, but this technique is not generally applied in the field as a practical solution to this problem. This form of corrosion displays itself as fingerlike or branching cracks in the stainless, often near welds.

It is important to note that SCC in general is a form of corrosion that affects many alloys, not just stainless steels. It requires tensile stress and an environment

specific to the alloy. Steel can suffer SCC in caustic solutions; brasses can suffer stress corrosion cracking in solutions containing ammonia. The British army in India back in the 1800s had a nasty experience with this form of corrosion damaging their brass ammunition. It was termed seasonal cracking, and made it difficult for them to keep their stiff upper lips.

With stainless steel, the susceptible environment is chloride in solution. There are some indications that oxygen plays a part as well. Chloride SCC of austenitic stainlesses such as 316 is generally not common at temperatures below approximately 50 °C (132 °F) to 60 °C (140 °F), or at those temperatures so hot that the surface stays dry. Even low chloride concentrations can be a problem, especially at areas of alternate wetting and drying where a salt deposit can form. Applied tensile stresses, forming stresses, or just residual weld stresses (ask any welder – he'll tell you how stressful his job is) can provide sufficient tensile stress to cause SCC. As noted earlier, duplex stainlesses, though they have a partial austenite microstructure, have a low nickel content and are rather resistant to chloride SCC; increasing the nickel content of the alloy above the levels in the 304 and 316 stainlesses (8 – 14%) can also decrease chloride SCC susceptibility, with virtually complete immunity once 30 – 40% nickel has been added (do you hear a cash register ringing?). SCC is very insidious; it is virtually impossible to determine when it will start and how quickly it will spread.

Rusty stainless steel? If you have a ferritic stainless exhaust system, you may have observed some darkening/rusting of the hot surfaces over time. However, even more highly alloyed stainlesses (and some other alloys, such as nickel alloys, in some cases – but we can save that for another time) may at times show rust streaks. This is usually attributable to the surface having been machined with steel tools or tools contaminated with steel. The result is that steel gets smeared onto or embedded into the stainless surface and subsequently rusts upon exposure to the elements; it is not really the stainless steel rusting. To prevent this phenomenon, stainless steels are sometimes given a passivating treatment, which is really a misnomer. A passivating treatment is basically an acid (e.g., a nitric acid) bath that dissolves out the imbedded iron, allowing a more perfect passive film to then form.

That pretty blue stain around the weld. Remember how your mother always told you that cleanliness is next to godliness? Much the same can be said of welding in general, and especially when it comes to welding stainless and other alloys. The stainless steel surface about a weld must be sufficiently shielded, otherwise the hot metal may react with the oxygen in the air and form a blue film. This blue film is basically a "thick" chromium oxide; unfortunately, the way it forms is by sucking up chromium from the alloy beneath. The result is a "thick" chromium oxide film full of defects and an alloy beneath that is, at least near the surface, poor in chromium and more susceptible to corrosion than it would otherwise have been. Proper shielding of the weld area (e.g., proper shielding gas flow when TIG welding (Tungsten Inert Gas or so-called Helli-Arc welding); adequate effect from the coating on a coated rod) should be ensured in the first place; if this is not

done, then the affected area should be pickled after welding to remove the blue and the layer of depleted alloy beneath. Grinding off the affected area may in some cases also be sufficient.

Why this "L" after the grade of stainless, and do I want it. An "L" is sometimes seen following a stainless grade number, as in the case of 304L or 316L. This means that, instead of having 0.08% carbon, the alloy has only 0.03% carbon. This may not seem like much of a difference, but it can have a significant impact. Specifically, the low carbon content can prevent a form of corrosion termed intergranular attack.

The cooling cycle involved in the usual welding of these stainlesses causes some of the chromium to react with carbon in the alloy and to precipitate out at the grain boundaries of the weld heat-affected zone (when metals and alloys solidify, they solidify as crystals that stop growing when the boundaries of crystal grains contact one another). What this means is that, in a certain area of the heat-affected zone of the weld, alloy grains loose chromium in a narrow band near their boundaries. The chromium carbide formed at the boundaries will tend to be more noble (less likely to corrode, more likely to induce galvanic corrosion of something else) than the nearby depleted alloy of a grain. In some environments, the result will be corrosion of the narrow depleted grain region with the remainder of the grain then dropping out since there is no metal left to hold it in place. This is known as intergranular corrosion and results in a sugary appearance of the metal at a distance about ¼ inch away from the edge of the weld bead. This can be avoided by properly heat-treating the affected area to resolutionize the carbon; however, sometimes this is not easily done. Reducing the carbon content of the alloy slows down the rate of formation of these carbides so that no significant carbide precipitation occurs under normal welding conditions. However, affecting one alloy parameter usually affects another as well; in this case, the penalty paid for preventing carbide precipitates by lowering the carbon content is a loss of about 3% in strength.

Remember how I said cleanliness is next to godliness in welding? Well, if a welder wipes the surface of an "L" grade stainless with an oily/greasy rag before welding, he'll drive the carbon in that oil/grease into the heated weld area, negating the benefits of the carbon reduction – similar to washing down a wall, then wiping it down with a dirty rag before painting.

Another way to avoid chromium carbides at the grain boundaries is to use stabilized grades of stainlesses. These include 321 (stabilized with titanium) and 347 (stabilized with niobium). The so-called stabilizers in these alloys scavenge up the carbon that would otherwise react with the chromium during welding; however, under certain thermal history conditions, these alloys can lead to another form of heat-affected zone corrosion called knife-line attack. Since the advent of low carbon grades, stabilized stainlesses aren't used that much anymore.

There's a 304/304L marking on my pipe elbow. Which is it? By adding some nitrogen to the alloy, metallurgists (a fancy word for today's college educated blacksmiths) have been able to recover much of the strength lost by lowering the carbon content to 0.03% (see immediately above). In short, this is low carbon 304L with controlled nitrogen addition for slightly greater strength.

Now that I've installed stainless parts, why do the remaining steel parts seem to corrode faster? As you may be aware, connecting different metals together in solution can cause one to corrode more quickly. This is termed galvanic corrosion. Stainless steels are typically more noble (i.e., less likely to corrode) than steel and will often cause steel to corrode preferentially (if they are electrically connected to steel and if the two are in a solution that touches them both). Do you suppose this was coincidental? Or, did the industry think of a cleaver way to induce customers to replace all connected parts in stainless steel too?

One interesting example (at least I think so) of this phenomenon is stainless automotive trim, often a 434 stainless. Although today's cars are sparse in their use of trim, or use plastic trim, you may recall bygone years when bright trim was in (i.e., groovy). In those days you may also recall that the steel auto-body near the trim would often rust and perforate. To a significant extent, this was because of galvanic action between the trim and the auto-body when the car got wet (especially if road salts were present). One solution to this problem that an innovative manufacturer provided was to clad the backside of the 434 with aluminum. The metallurgically bonded aluminum cathodically protected the auto-body steel. However, metallurgically bonding stainless steel and aluminum is not as easy as it sounds. Stainless steel and aluminum can't be welded together because brittle aluminum intermetallics form, causing the bond to "unzip" and come apart when one tries to bend or form the clad metal. You need a very clean surface between the two metals and about a million pounds per square inch to force the atoms of metal together while cold and special heat treatments to then maximize bond. Don't try this at home.

Summary

I hope this clears up some of your questions regarding stainless steels. As you can see, there's much to consider. Stainless steel is not a single alloy but a family of alloys that can be divided into five major groups. Which particular stainless you choose will depend on such factors as what you want the part to do, the fabrication processes it will undergo, and the environment to which that part will be exposed. Also, you will need to consider the cost involved. If you need a stainless that's hard and will hold a sharp edge for slitting or cutting, then a properly heat-treated martensitic stainless, like 420, or even a precipitation hardening stainless, may best suit your needs. If a high level of corrosion protection in an aggressive environment is your chief concern, then one of the

austenitics may be more likely to meet your needs. If one of the common work horses such as 304L or 316L won't, then perhaps something with a higher alloy content will do so—you may even want to consider one of the non-standard or proprietary grades. If you will be welding on that part, then these austenitic stainlesses may also be a good choice as they are relatively easy to weld; however, pay special attention to selection of the weld rod. For instance, while, as you might expect, 316L is normally welded using 316L weld rod, 304L is normally welded using 308L rod material; then again, superaustenitics like AL6XN should be welded with a high nickel alloy rod, such as 625 or C276. You may also want to consider one of the duplex grades, such as 2205, for good corrosion resistance and strength; however, you will need a much more sophisticated and experienced welder if you plan to weld on this alloy, and you may need to do more extensive qualification tests and followup quality testing. Finally, you will also need to consider the other metals to which you are connecting the stainless part; stainless can't be welded to every metal, and stainless may cause galvanic corrosion.

For additional assistance please contact your friendly neighborhood Materials Engineer at the Bureau of Reclamation, Technical Service Center. He can help you select a stainless steel to meet your needs and recommend testing to verify that the alloy has sufficient corrosion protection for your environment. A good source of reading material on the subject of stainless steels, if you are genuinely interested, or if you want a good night's sleep, is the 500-page plus ASM (American Society for Metals, International) Specialty Handbook, *Stainless Steels* (apparently metallurgists have big hands). Please keep in mind that a little knowledge can be a dangerous thing.

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Please send corrosion related questions you would like Rusty Fingers to answer in this publication to "Dear Rusty," C/O Roger Turcotte, Materials Engineer, Bureau of Reclamation, Technical Service Center; e-mail: rturcotte@do.usbr.gov, or call 303-445-2383 for immediate assistance.